Jim C. Comments to SRC on ISTM Tech Memo 6/18/02

1. General comment – I recommend we go through and eliminate qualifiers such as "very" or "only" unless it is completely clear they are deserved. Simply state "...would have been correct in 62% of the cases" as opposed to "...would have been correct in *only* 62% of the cases.

2. I think we should include a section or at least brief discussion on quartz PE samples. Even though these are of limited value, we should discuss the results and whatever interpretation of them we made.

3. Page 2. Why were DFC soils chosen by USGS? As it reads it appears random (ie any soil could have been used), but in reality it was chosen because it had similar characteristics to Libby soil.

4. Page 3. Libby Soil Matrix ISTM Samples. 2nd sentence. The four samples were collected because they had lower concentrations of fibrous or non-fibrous amphibole or both? Typo "that" in same sentence.

5. Page 4. Section 3. We need a little more discussion on SOPs here. First, we need a copy of the exact SOP/method that both EMSL/RESI used when they analyzed these samples. I would prefer we put them in as an appendix or attachment. Second, we should point out that an intended potential benefit of this exercise was providing information that may help refine the SOPs. Lastly, I think it would be helpful to briefly explain the methods in this section. For instance, it is important to know that the IR method used by EMSL also contains a limited, non-quantitative PLM step – it isn't spectroscopy completely alone.

6. Page 4, Setion 4.1 I suggest we should insert a Table 2, similar format to Table 1, with actual numerical results.

7. Page 4, Section 4.1. Under SEM analysis, I think it is misleading to state "...DFC soils spiked with coarse fibers..." and "...fine-ground fibers." The samples were spiked with course ground *material* or fine ground *material*, not course or fine ground fibers. We can't say exactly how the spike prep affected fiber size distribution, and I don't want to imply for instance that the coarse ground spikes contained no small fibers – it is certain they did. We can say that the fine ground material was likely reduced only to small fibers, though the size distribution is unknown. I think we can also say that the coarse material likely had a combination of larger materials and various fiber size materials. Might want to discuss this back in Section 2 also.

8. Page 6, Section 4.1, 1st paragraph. Change sentence to: "Rather, the current program at Libby is of a "screening" nature and seeks to classify..."

9. Page 7, paragraph at top. In the semi-quantitative analysis, it is important to note 3 things. (1) The EMSL IR method includes a PLM step, and the PLM did not see any LA in the Bin B DFC fine either. This is important because it shows we likely wouldn't have obtained better or different results with our "current" soil screening method of PLM. The fibers were (a) of a size nature and (b) distributed through the sample such that they didn't produce strong enough spectra to be detected and were too small and apparently well-spaced to be seen with the resolving power of the PLM. (2) We should note that for the one DFC fine sample in Bin C, IR did not miss it and properly characterized it. (3) Lastly, while IR reported ND for all of the Bin B DFC fines, SEM did not. While the quantification was not good, the method at least detected some material in some samples - EMSL detected them and properly characterized them at a 44% rate. While this isn't great, it appears to at least be better than PLM or IR.

10. Page 7, paragraph before Section 5. Please do the other two bins for PLM concordance as well.

11. Section 5. We may not want to change the text too much here, but I wanted to address the limited results of the study and how it affects my decision making The range I was most interested in evaluating at this stage was Bin B. This gets back to the email I sent to CDM a few days ago regarding false positives and false negatives. I won't reiterate all of that here. But in general, the most

important mistake I don't want to make at this screening stage is to have something in the Bin B range and put it in Bin A – a false negative. For both the course ground sample sets, SEM at both labs avoided this pretty well (39/44 = 89%). IR was similar (15/17 = 88%). (As an aside, I don't have the data in front of me, but I seem to recall the false negatives were generally for samples in the .1-.3 range, on the lower end of the spectrum) **So, while this data set has limited value in some respects, it was of great value for my most important decision criteria.** This shouldn't be lost in the text and it as provided me enough information to at least move forward for now. It showed me that for course ground material, material I think is closest to the reality of what we see in Libby, the methods met my most important objective. Further analysis can reinforce that, but more importantly it will help evaluate some of my less important decision criteria (e.g. false positives or negatives around the 1% cutoff, or False positives around the .1% cutoff and the whole background issue). This will help me properly interpret the data we get for actual samples we are collecting now.

12. On the graphs, especially IR, is there any way to differentiate visually between a <.1% and a =.1%? I think these all fall on the same line on the IR graph, and they obviously mean totally different things. I would at least put the <'s below the LRL.

DRAFT

TECHNICAL MEMO

SUMMARY AND EVALUATION OF PRELIMINARY SOIL TEST MATERIAL SAMPLE ANALYSIS

1.0 INTRODUCTION

USEPA Region 8 is currently engaged in a program to test and evaluate a variety of analytical methods for quantification of asbestos in site soils, vermiculite insulation, and other related site samples. As part of this program, an initial pilot study was performed using a set of "interim soil test materials" (ISTMs) with the aim of allowing a rapid initial assessment of the relative performance of infrared spectrometry (IR) and scanning electron microscopy (SEM) to quantify soil concentrations in the range of 0.1% to 5%.

2.0 ISTM PREPARATION

ISTM samples used in this pilot study consisted of two different types: soils spiked by USGS with known mass percents of Libby amphibole material, and authentic Libby field soil samples. These two sample groups are described below.

2.1 Spiked Samples Prepared by USGS

Spiked ISTM samples were prepared by USGS in concentrations ranging from 0.1 weight percent (%) up to a maximum of 0.8% asbestos using soil material collected from a site in the Libby, Montana area and a single soil sample collected from the Denver Federal Center (DFC) in Lakewood, Colorado. The collection, preparation and mixing of these materials is described below.

Amphibole Spiking Material

Amphibole material used to spike these soil matrices was obtained from a composite of ore samples collected from six locations at or near the Libby, Montana vermiculite mine site. The six samples were selected for this work because USGS analysis of their mineralogical

composition found that they were highly enriched in asbestos, contained the full range of amphibole types found at the Libby site, and were relatively free of contaminants (based on XRD analysis). The composite sample was coarse ground using a three inch horizontal grinder equipped with steel plates. Approximately half the batch was later wet ground in a four liter ball mill using corundum grinding cylinders (1") to produce a fine grained aliquot. Both this coarse and fine grained form were used in the preparation of ISTM samples.

DFC Soil Matrix ISTM Samples

I think quartz samples should be discussed.

Soil collected from the Denver Federal Center (DFC) was collected from a site chosen at random from an area located on the south east section of the center. During collection an area approximately one square meter in size was cleared of all surface debris and the top 3 inches of grass removed. Sufficient soil was removed to a depth of approximately eight inches to fill a five gallon plastic bucket (50 lbs). The soil was oven dried at room temperature in plastic lined cardboard trays (12x24x2 in). After drying the soil was processed through the USGS soil dissagregator and then passed over a 2 mm screen. Material passing the screen was collected for use in the soil test sample preparation. The soil material is dark brown in color, contains minor amount of fibrous organic material, and small pebbles (<2mm).

Why DFC chosen?

Approximately 2500 g of DFC soil was transferred to one gallon container fitted with a plastic mixing card. The soil sample was mixed for f our hours and then split into 500 g aliquots using a standard Jones splitter. Each aliquot was transferred to a 1-liter wide mouth glass container. Aliquots of fine and coarse grained Libby amphibole material were added (HEPA hood) to each container in order to obtain amphibole concentrations of 0.1, 0.3, 0.6, 0.8 weight percent (%). An aliquot of the DFC soil was not spiked with amphibole and serves as a blank material. The amphibole aliquots were added to the soil as aqueous suspensions along with approximately 500 ml of deionized water. The container was sealed, vigorously shaken for approximately five minutes, uncapped, and then mixed using an overhead stirrer for approximately 1 hour. After mixing the slurry was quantitatively transferred to a 9 x 14 x 1 inch metal tray lined with aluminum foil. The tray was placed on a hot plate and allowed to dry over night at ~90C. The next day the sample was hand ground using a two liter ceramic mortar and pestle. The mixture of coarse and fine grained soil material was returned to its original 1 liter glass bottle (cleaned and dried) which was fitted with a plastic mixing card. The container was sealed, transferred to a horizontal roller and mixed for approximately two hours. After mixing aliquots (~20g) were

removed from the container using a sample thief and transferred to one ounce glass bottles. The bottles were labeled with a code identifying the soil used in the preparation, amphibole concentration, and texture of the amphibole (fine, coarse) used.

Libby Soil Matrix ISTM Samples

Soil material from the Libby, Montana area used in the preparation of these test samples was collected from four locations in the Libby area. The four samples were selected for use because the USGS found they had lower concentrations of amphibole that other soil samples from Libby. The samples were light brown in color, contained a minimal amount of visible fibrous organic material and were easily disaggregated. The four soil samples were transferred to a new one gallon cardboard container fitted with a customized plastic mixing card. The container was covered, sealed with tape and then transferred to a horizontal roller apparatus where it was mixed for a total of six hours. After mixing the sample was split by hand into three 500 g aliquots in a HEPA hood. Each aliquot was transferred to a one liter wide mouth glass jar.

[INSERT NEEDED ON "PREPARATION" (GRINDING AND SIEVING) OF LIBBY SOILS]

To each soil aliquot a separate amount of coarse ground Libby amphibole was added wet. A total of 200 ml of deionized water was then added to the jar and the amphibole/soil mixture was mechanically mixed using a overhead stirred equipped with a customized stirrer. The sample was mixed for a total one hour. The sample was then quantitatively transferred to a 9 x 14 x 1 inch metal tray lined with aluminum foil. The tray was placed on a hot plate stirred to evenly distribute the mixture and then allowed to dry overnight at ~90C. The next day the dried sample was lightly ground using a 2 L ceramic mortar and pestle. The sample was then transferred back into its original one litter wide mouth glass container which had been fitted with a plastic mixing card. The sample was then mixed for two hours using the horizontal roller. Individual samples (20g) were removed from the container using a sample thief and transferred to one ounce glass bottles. The bottles were labeled with a code identifying the soil used in the preparation, amphibole concentration, texture of the soil (fine, coarse). Amphibole concentration in Libby soil samples had concentrations of 0.2, 0.65, 0.8 weight percent.

2.2 Unspiked Libby Field Samples

The ISTM data set also contained a number of authentic soil field samples from Libby. These were selected for inclusion in the pilot evaluation based on the PLM results for the samples. These samples are summarized below:

PLM Result	Number of samples
ND	4
Trace	3
Quant (1%-5%)	5

Need a little elaboration here especially in regard to IR.

3.0 ANALYSIS

One set of 38 samples was sent to each of two laboratories: EMSL Analytical, Inc. (EMSL), and Reservoirs Environmental Analytical Services (RESI). These samples are summarized in Table 1. EMSL analyzed samples by infrared spectroscopy (IR) and by scanning electron microscopy (SEM), while RESI analyzed the samples by SEM. The details of the analytical methods are specified by the project-specific SOPS developed for this project.

4.0 RESULTS AND DISCUSSION

4.1 Quantitative Analysis

Need table with actual results.

SEM Analysis

Figure 1 summarizes the SEM results from EMSL (upper panel) and RESI (lower panel) for the ISTM samples spiked with known amounts of asbestos by USGS. Inspection of these figures reveals that both laboratories tended to underestimate the spiked mass percent. The underestimation tended to be less for DFC soils spiked with coarse fibers, and greatest for DFC soil spiked with fine-ground fibers. The reason for the understimation is not known.

coarse fibers? wording

Figure 2 summarizes the SEM results from EMSL and RESI for authentic field samples from Libby. The value plotted on the x-axis is the mass percent by PLM, which may not be an

accurate reflection of the true concentration in all cases. For convenience, values reported as "ND" by PLM are plotted at an assumed concentration of 0.05%, and samples reported as "<1%" (Trace) by PLM are plotted at an assumed concentration of 0.5%. As seen, agreement between SEM and PLM is very poor, with SEM tending to report substantially lower concentrations than PLM. The basis for this discrepancy is unknown, but could result either from a tendency to under-report by SEM and/or a tendency to over-report by PLM.

Figure 3 provides an inter-lab comparison of SEM results from EMSL and RESI. The correlation coefficient (R) and the coefficient of determination (R^2) are as shown below:

Sample Type	R	R^2
Spiked DFC (Coarse)	0.370	0.137
Spiked DFC (Fine)	0.993	0.986
Spiked Libby (Coarse)	-0.264	0.070
Unspiked Libby	0.886	0.785

As seen, correlation is relatively poor for samples spiked with coarse fibers. The correlation appears to be better for samples spiked with fine-ground fibers and for Libby field samples, but this is an artifact stemming from the fact that most of these samples were at or near the detection limits for both laboratories.

IR Analysis

Figure 4 presents the results of IR analysis by EMSL of the USGS spiked samples (upper panel) and the unspiked Libby field samples (lower panel). Note that the IR results are bounded between a lower reporting limit of 0.1% and an upper reporting limit of 1.0%.

As seen, there is a general tendency for IR to underestimate the concentration of asbestos in both data sets. The basis of the underestimation is not known.

4.1 Semi-Quantitative Analysis

It is important to realize that the current program of soil investigation at Libby does not necessarily require precise quantification of asbestos levels in soil to support decision-making. Rather, the current program at Libby seeks to classify each soil sample into one of three bins:

Bin	Concentration Range
A	< 0.1%
B	0.1-0.9%
C	≥ 1%

A concordance analysis based on this binning system is presented in Table 2 for SEM, and in Table 3 for IR. In all cases, analytical results were rounded to the nearest 0.1% before assignment to bins.

Concordance by SEM

As seen in Table 2, if the USGS spiked samples had been assigned to bins based on SEM, assignment would have been correct in only 50%-77% of the cases. However, most of the errors were due to the inability to detect the fine-grained spiking material in DFC soils. If this set of samples is excluded, the assignment to bins would have been 71%-94% accurate. When mis-classification errors occurred, the majority of errors were to underestimate the true concentration, assigning the sample to a lower concentration bin than appropriate.

The last entry in Table 2 shows the degree of concordance for samples whose concentration was quantifiable (≥ 1%) by PLM (this corresponds to bin C). As seen, concordance was very low in this case (0%-40%), with SEM tending to provide a lower concentration estimate than PLM. As noted above, it is not known whether this is because SEM is tending to underestimate and/or because PLM is tending to overestimate true concentrations.

Concordance by IR

As seen in Table 3, if the USGS spiked samples had been assigned to bins based on IR,

assignment would have been correct in ~~only~~ 62% of the cases. However, most of the errors were due to the inability to detect the fine-grained spiking material in DFC soils. If this set of samples is excluded, the assignment to bins would have been 88% accurate. When mis-classification errors occurred, all of the errors were to underestimate the true concentration, assigning the sample to a lower concentration bin that appropriate.

The last entry in Table 3 shows the degree of concordance for samples whose concentration was quantifiable (≥1%) by PLM (this corresponds to bin C). As seen, concordance was ~~about~~ 60%, with IR classifying 3 of 5 samples as being at or above 1%.

5.0 RECOMMENDED FOLLOW-UP

The data from this initial pilot study suggest that neither IR nor SEM are well suited to precise quantification of asbestos levels in soil, although both SEM and IR may be suitable for use in a semi-quantitative fashion. However, the results of this study are limited by a number of factors, including the following:

- The range of asbestos concentrations in the test materials spanned a relatively narrow range, limiting the ability to assess the performance of the methods. In particular, with regard to tests on semi-quantitative binning success, 25 out of 26 of the USGS-spiked samples were within bin B, with only one sample in bin C. There were five Libby site soils ranked by PLM as having quantifiable concentration values of 1% or above, but since the PLM results themselves are uncertain, it is not known how many of these samples were authentic bin C samples.

- No unspiked samples of DFC soil or prepared Libby soil were included, preventing a clear determination of the lowest levels that can be distinguished from background by each method.
- The Libby soil used to prepare spiked samples was ground and sieved, and both analytical laboratories indicated the soil matrix in these samples was un-representative of authentic Libby field samples.

Table 4 presents a suggested protocol for a follow-on study to help address these limitations.

Specifically, this study does not used ground Libby soil, spans a wider range of concentration values with multiple samples in each bin category, and does include unspiked soils. Only Libby soil (unground) is used as the spiking medium, and emphasis is placed on the coarse-ground spiking material since this is more likely to represent what is in most site soil samples than the fine ground materia. The results from this study or a study of similar design will be very helpful in obtaining additional information on the quantitative and semi-quantitative performance of IR and SEM for analysis of Libby soils.

TABLE 4. RECOMMENDED PROTOCOL FOR ADDITIONAL STUDY

Soil Matrix	Spiking Material	Approximate Spiking Level	Bin	Approximate Number
Libby soil (minimal amphibole content, coarse sieved but not ground)	Libby amphibole (coarse ground)	None	A	3-4
		0.02%		3-4
		0.06%		3-4
		0.2%	B	3-4
		0.6%		3-4
		2%	C	3-4
		6%		2-3
	Libby amphibole (fine ground)	None	A	3-4
		0.2%	B	3-4
		2%	C	2-3

In-sample heterogeneity
— Best effort analyze ×100

TABLE 1. SUMMARY OF ISTM SAMPLES

USGS ID Number	Libby Number	PLM Conc	Spike Mass %	Soil Type	Spike material	Sent To	
						EMSL	RESI
GSCD0A11			0.1	DFC	Coarse	x	x
GSCD0A60			0.6	DFC	Coarse	x	x
GSCD0B10			0.1	DFC	Coarse	x	x
GSCD0B32			0.3	DFC	Coarse	x	x
GSCD0C31			0.3	DFC	Coarse	x	x
GSCD0D82			0.8	DFC	Coarse	x	x
GSCD0F61			0.6	DFC	Coarse	x	x
GSCD0F81			0.8	DFC	Coarse	x	x
GSFD0011			0.1	DFC	Fine	x	x
GSFD0012			0.1	DFC	Fine	x	x
GSFD0031			0.3	DFC	Fine	x	x
GSFD0032			0.3	DFC	Fine	x	x
GSFD0060			0.6	DFC	Fine	x	x
GSFD0061			0.6	DFC	Fine	x	x
GSFD0081			0.8	DFC	Fine	x	x
GSFD0082			0.8	DFC	Fine	x	x
GSFDD02			2	DFC	Fine (dry mix)		x
GSFDDA2			2	DFC	Fine (dry mix)	x	
GSCL0A20			0.2	Libby bkg (milled)	Coarse	x	x
GSCL0A80			0.8	Libby bkg (milled)	Coarse	x	x
GSCL0A81			0.8	Libby bkg (milled)	Coarse	x	x
GSCL0B22			0.2	Libby bkg (milled)	Coarse	x	x
GSCL0C66			0.65	Libby bkg (milled)	Coarse	x	x
GSCL0D65			0.65	Libby bkg (milled)	Coarse	x	x
GSCL288			0.8	Libby bkg (milled)	Coarse	x	x
GSCL465			0.65	Libby bkg (milled)	Coarse	x	x
GSCL802			0.2	Libby bkg (milled)	Coarse	x	x
GSS0943C	1-00943	ND		libby soil #0943	None	x	x
GSSA00108	A00108	ND		libby soil #108	None	x	x
GSSA00112	A00112	ND		libby soil #112	None	x	x
GSS103813	1-03813	ND		libby soil #3813	None	x	x
GSSA00107	A00107	Trace		libby soil #107	None	x	x
GSSA00110	A00110	Trace		libby soil #110	None	x	x
GSS103806	1-03806	Trace		libby soil #3806	None	x	x
GSS0942C	1-00942	1		libby soil #0942	None	x	x
GSSA00109	A00109	1		libby soil #109	None	x	x
GSS103808	1-03808	1		libby soil #3808	None	x	x
GSDM001	1-04152	3		Libby Soil (CDM)	None		x
GSDM002	1-04152	3		Libby Soil (CDM)	None		x
GSDM003	1-03407	5		Libby Soil (CDM)	None	x	
GSDM004	1-03407	5		Libby Soil (CDM)	None	x	

TABLE 2. CONCORDANCE FOR SEM

DFC Coarse	Nominal	EMSL			RSEI		
		Bin A	Bin B	Bin C	Bin A	Bin B	Bin C
Bin A	0						
Bin B	8	1	7		2	5	1
Bin C	0						
Concordance		88%			63%		

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DFC Fine	Nominal	EMSL SEM			RSEI		
		Bin A	Bin B	Bin C	Bin A	Bin B	Bin C
Bin A	0						
Bin B	8	4	4		8		
Bin C	1		1				1
Concordance		44%			11%		

Libby Coarse	Nominal	EMSL			RSEI		
		Bin A	Bin B	Bin C	Bin A	Bin B	Bin C
Bin A	0						
Bin B	9		9		2	7	
Bin C	0						
Concordance		100%			78%		

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All Spiked samples	Nominal	EMSL			RSEI		
		Bin A	Bin B	Bin C	Bin A	Bin B	Bin C
Bin A	0	0	0	0	0	0	0
Bin B	25	5	20	0	12	12	1
Bin C	1	0	1	0	0	0	1
Concordance		77%			50%		

All except DFC Fine	Nominal	EMSL			RSEI		
		Bin A	Bin B	Bin C	Bin A	Bin B	Bin C
Bin A	0	0	0	0	0	0	0
Bin B	17	1	16	0	4	12	1
Bin C	0	0	0	0	0	0	0
Concordance		94%			71%		

Field Samples Unspiked	Nominal	EMSL			RSEI		
		Bin A	Bin B	Bin C	Bin A	Bin B	Bin C
Bin C	5	1	4		1	2	2
Concordance		0%			40%		

Bins
A = less than 0.1%
B = 0.1% to 0.9%
C = greater than or equal to 1%

TABLE 3. CONCORDANCE FOR IR

what concentrations were tested?

DFC Coarse	Nominal	EMSL IR Bin A	Bin B	Bin C
Bin A	0			
Bin B	8	1	7	
Bin C	0			
Concordance		88%		

DFC Fine	Nominal	EMSL IR Bin A	Bin B	Bin C
Bin A	0			
Bin B	8	8		
Bin C	1			1
Concordance		11%		

Libby Coarse	Nominal	EMSL IR Bin A	Bin B	Bin C
Bin A	0			
Bin B	9	1	8	
Bin C	0			
Concordance		89%		

All Spiked samples	Nominal	EMSL IR Bin A	Bin B	Bin C
Bin A	0			
Bin B	25	10	15	
Bin C	1			1
Concordance		62%		

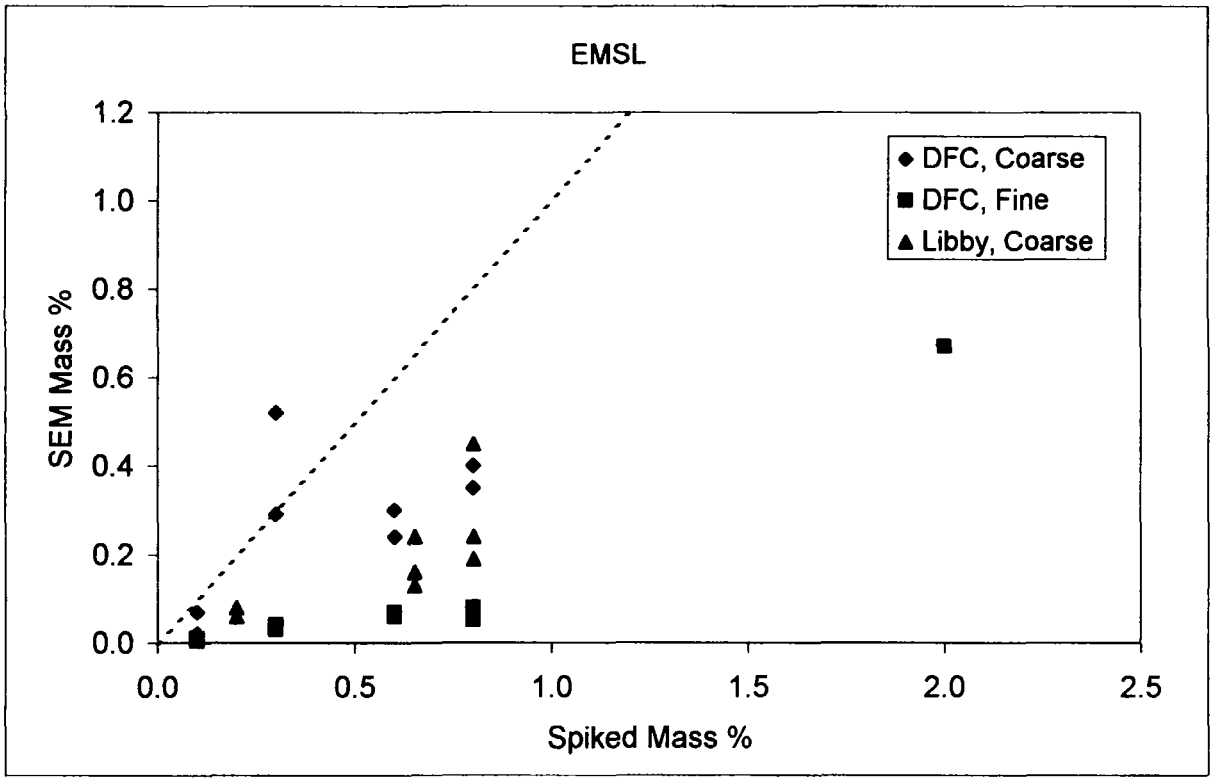
All except DFC Fine	Nominal	EMSL IR Bin A	Bin B	Bin C
Bin A	0	0	0	0
Bin B	17	2	15	0
Bin C	0	0	0	0
Concordance		88%		

Field Samples Unspiked	Nominal	EMSL IR Bin A	Bin B	Bin C
Bin C	5		2	3
Concordance		60%		

Bins

A = less than 0.1%
B = 0.1% to 0.9%
C = greater than or equal to 1%

FIGURE 1. SEM RESULTS FOR USGS SPIKED ISTM SAMPLES



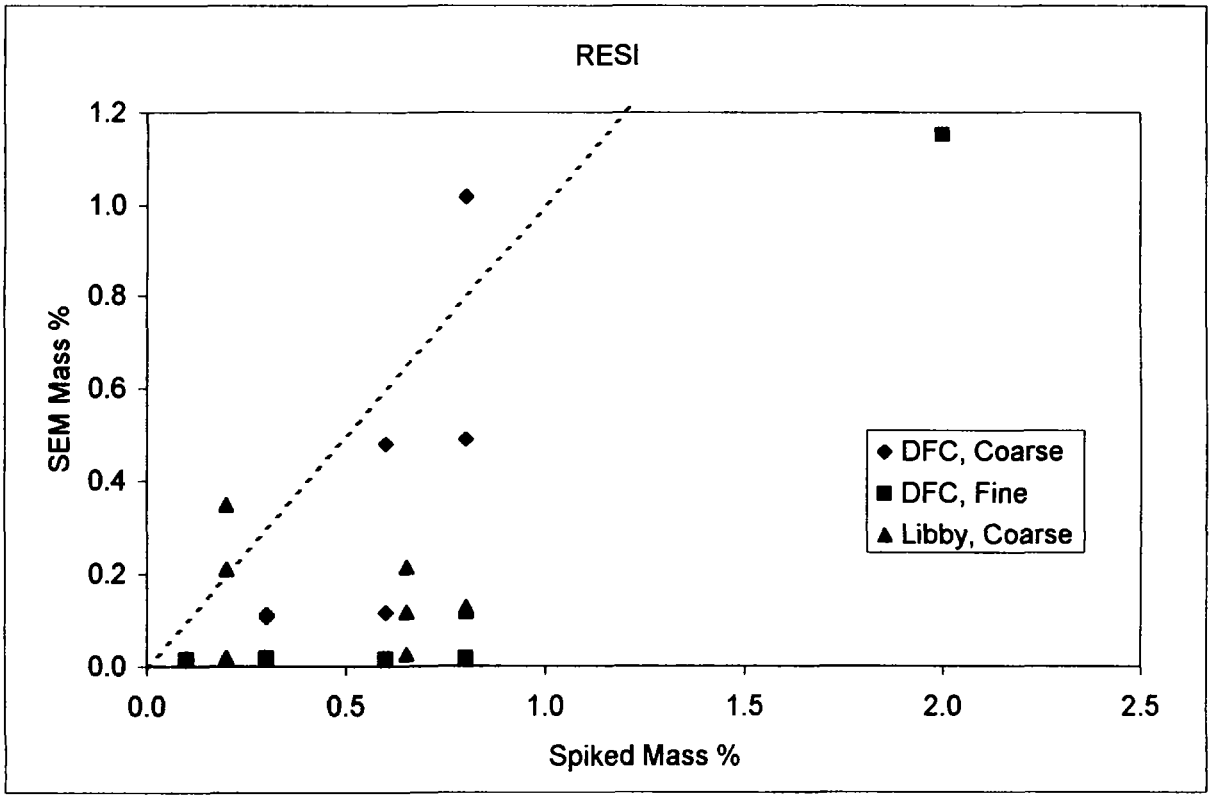
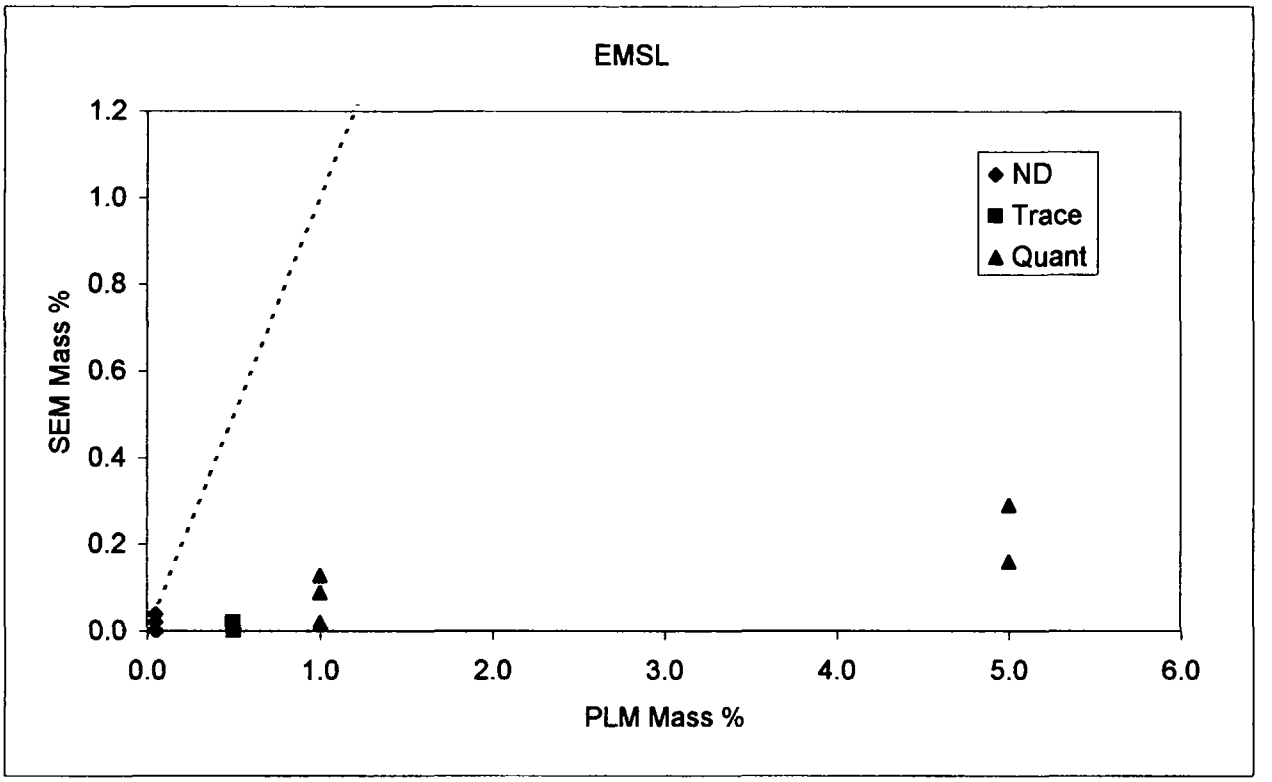


FIGURE 2. SEM RESULTS FOR LIBBY FIELD SAMPLES



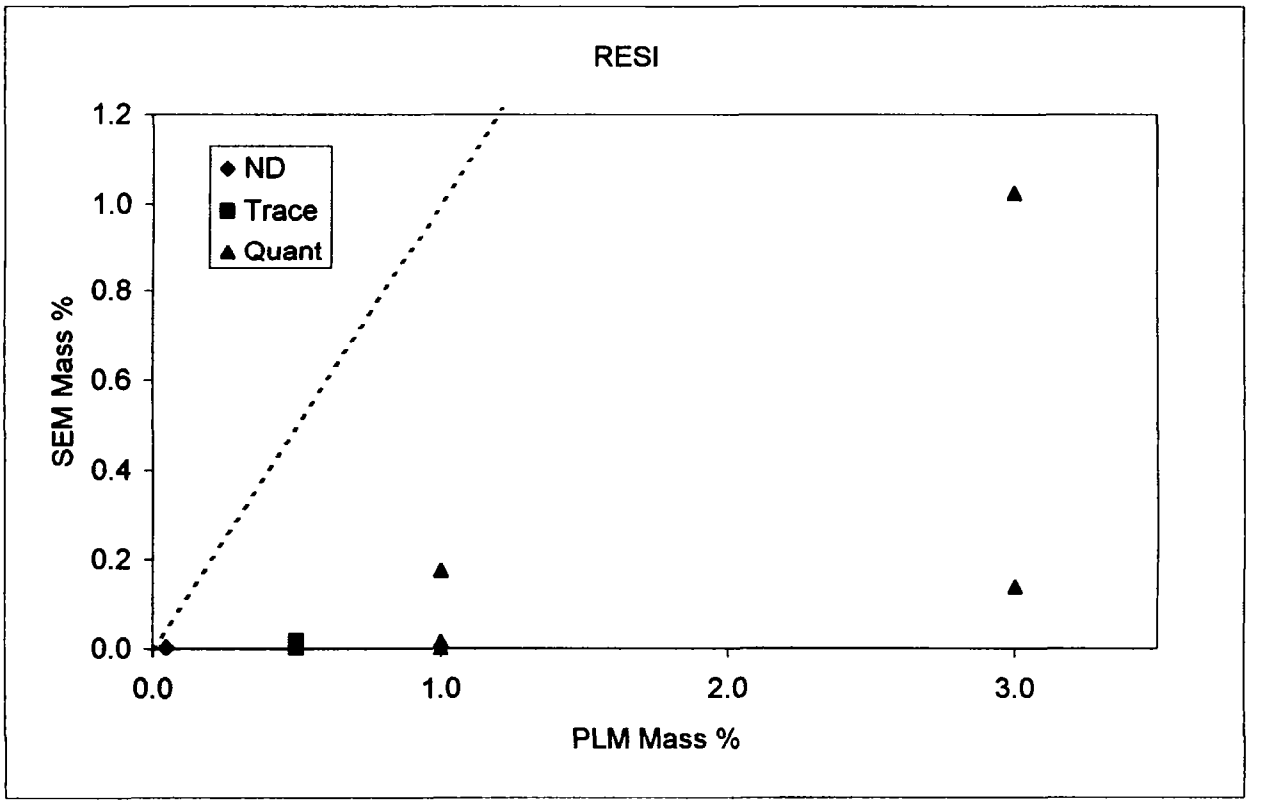
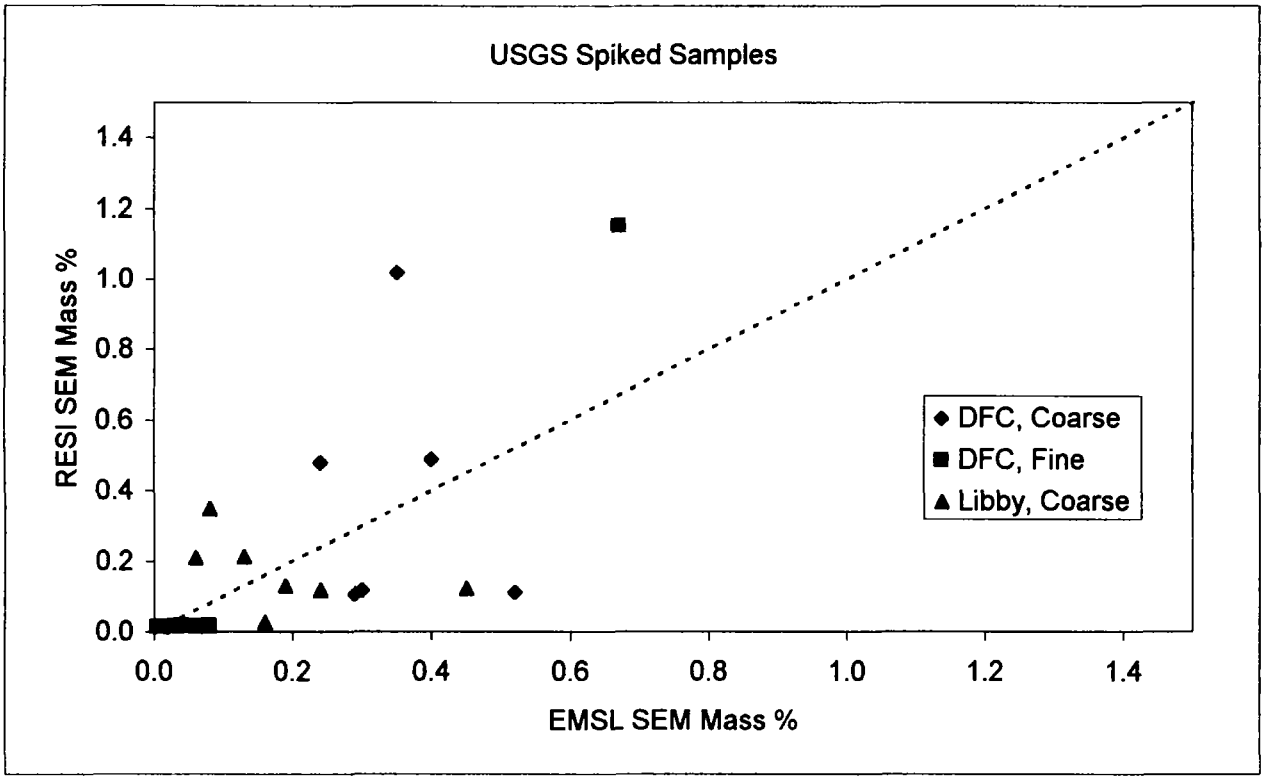


FIGURE 3. INTERLAB COMPARISON OF SEM RESULTS



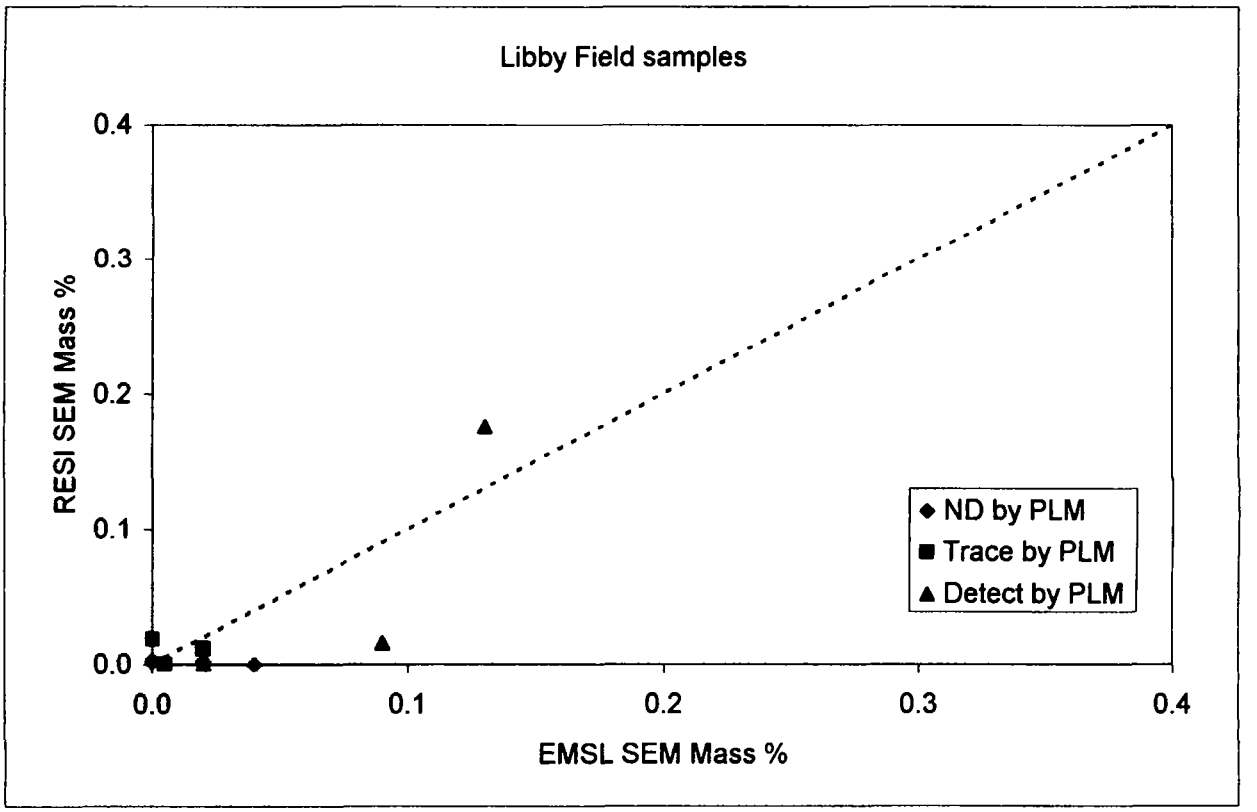


FIGURE 4. IR RESULTS (EMSL)

Can't tell difference between = .1% and < .1%